

## **GRAFTED POLYELECTROLYTE MEMBRANES FOR LITHIUM BATTERIES AND FUEL CELLS.**

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Polyelectrolyte materials have been developed for lithium battery systems in response to the severe problems due to salt concentration gradients that occur in composite electrodes (aka membrane-electrode assemblies). Comb branch polymer architectures are described which allow for grafting of appropriate anions on to the polymer and also for cross-linking to provide for appropriate mechanical properties. The interactions of the polymers with the electrode surfaces are critical for the performance of the system and some of the structural features that influence this will be described. Parallels with the fuel cell MEA structures exist and will also be discussed.

## **Lithium Batteries for Transportation and High Energy Density Applications (e.g. Satellites and Aerospace).**

The successful introduction of the Hybrid Gas-Electric cars such as the Toyota Prius and Honda Civic illustrate the on-going need for new and better large battery systems which will become even more pressing in the event of successful development of PEM fuel cells for transportation. Hybrid fuel cell-electric systems will be even more dependent on the battery performance for cold-start and peak power. The Hybrids presently use Nickel metal hydride batteries which are too expensive for general use and there is a need for less expensive battery technology for this high power application as well as for electric vehicle (EV) applications where the vehicle is driven solely under battery power for significant periods. Adaptation of the successful Li Ion battery technology commonly found in lap-top computers and cell phones seems to be a logical progression for these transportation applications as the Li Ion systems not only possess higher power but also higher energy densities expressed in both weight and volume. However, development of large batteries has been impeded by a perception of safety problems related to the volatile and flammable organic liquids used in the electrolyte. This perception has been intensified by reports of gas venting on charge at elevated temperatures resulting from reactions of the carbonate electrolytes. Such reports are also not welcome for the application of Li Ion technology for use in satellites where gas venting could cause significant problems. Lithium ion battery systems are very attractive for aerospace applications due to their low weight. For both transportation and aerospace applications a wide operating temperature is desired. The advantages of liquid electrolytes fade as the temperature drops below  $-40^{\circ}\text{C}$  as the increasing viscosity reduces the power of the battery.

The alternative form of lithium battery is the lithium-polymer battery which involves a lithium metal electrodes and a metal oxide cathode material separated by an ionically conducting but electronically insulating polymer membrane which contains no volatile or flammable liquids. The typical membrane used for the last twenty years has been polyethylene oxide (PEO) in which is dissolved a lithium salt such as lithium triflate ( $\text{Li SO}_3\text{CF}_3$ ) or Lithium TFSI ( $\text{Li N}(\text{SO}_2\text{CF}_3)_2$ ). In this system the lithium ions are solvated by the ether oxygens of the polyether chains and the ions move due to the segmental motion of the polymer chains in the amorphous form as the transport properties of the lithium ions in the polymer improve as the polymer glass transition temperature is lowered. Although there may be ionic motion through crystalline phases this is relatively small. The large TFSI anion appears to be more fully dissociated from the lithium ion than the triflate ion leading to better transport properties. However, even with LiTFSI, the transport properties of PEO do not allow EV performance below  $85^{\circ}\text{C}$ [1] and much effort has gone into finding polymer systems that will work at lower temperatures[2].

The second important drawback of the lithium-polymer system is caused by dendrite growth at the lithium metal electrode. Dendrite growth is a consequence of an electrode function that involves plating of metal, in this case lithium. The dendrite, once initiated, grows through the membrane to the other electrode and causes an electrical short circuit and killing the battery. In less severe cases, the dendritic growth leads to the formation of “mossy” lithium, which poses a safety problem. Dendrite growth is certainly related to the lithium ion transport properties but may be inhibited by membranes with appropriate mechanical properties which can restrain the initiation. High moduli in the polymers tends to be counter to the polymer properties needed for

good transport properties and this is illustrative of the difficulties in designing a polymer membrane for lithium batteries. This paper will give a brief overview of some of the problems associated with polymer electrolytes and suggest some designs for polyelectrolyte membrane that may overcome some of these difficulties. Some preliminary results are given.

### Binary salt systems.

In a binary salt polymer electrolyte system, both anions and cations are mobile. To describe the system, three transport properties are required and these are usually conductivity, salt diffusion coefficient and transference number. Since there is only an electrode reaction for the lithium ions, salt concentration gradients build up. The transference number of the anion indicates how strong is the tendency for salt accumulation under the effect of the current and the diffusion coefficient indicates how rapidly the system is able to relax the salt concentrations[3] Figure 1 is a schematic of salt concentration polarization that occurs in membranes and composite electrodes. It can be seen that the concentration polarization leads to a limit on the thickness of the composite electrode that can be accessed. Transport properties also vary as function of salt concentration and location in the cell. For example, the composite cathode consists of polymer-salt filled with carbon black nano-particles (10-20% loading) and active cathode particles (1-10  $\mu\text{m}$ ). Consequently, the segmental motion of the polymer is inhibited in the regions close to the electrode surfaces[4] leading to much different transport properties. Salt concentration gradients build up in the composite cathode and need time to relax between cycles. If salt diffusion coefficient is not high enough to allow the cell to relax, capacity fading occurs (1,2).

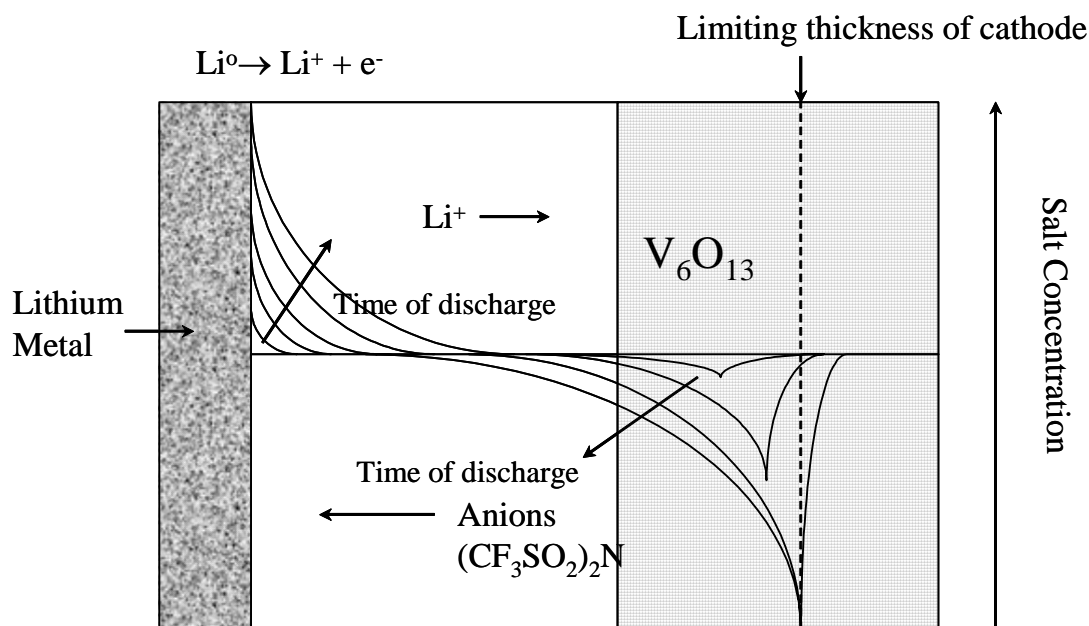


Figure 1. Effect of  $D_s$ ,  $t_+^0$  on Cell Performance. Concentration profiles lead to limited power & energy densities. Lack of a reaction for the anions leads to concentration polarization unless anion is immobilized ( $t_+^0=1$ ).

One can also see that the concentration of salt next to the lithium electrode can increase to high levels. It has been shown that the  $T_g$  of polymer electrolytes increases as the salt concentration increases and consequently the conductivity decreases precipitously as the discharge proceeds. Figure 2 shows conductivity plots and plots of  $T_g$  of various polymers as a function of salt (LiTFSI) concentration. The polymer structure in this case is a comb branch structure with a polypropylene oxide backbone and side chains of varying lengths which contain different ether groups[5, 6]. The ether groups are either ethylene oxide (EO) or trimethylene oxide (TMO). One can see a dramatic effect of the TMO groups on the  $T_g$  values as salt concentration increases and this affects conductivity at low temperatures, although there seems to be little effect at higher temperatures. However, the implication is clear that the TMO-containing polymers will suffer much less than the ethylene oxide polymers from the effects of salt concentration.

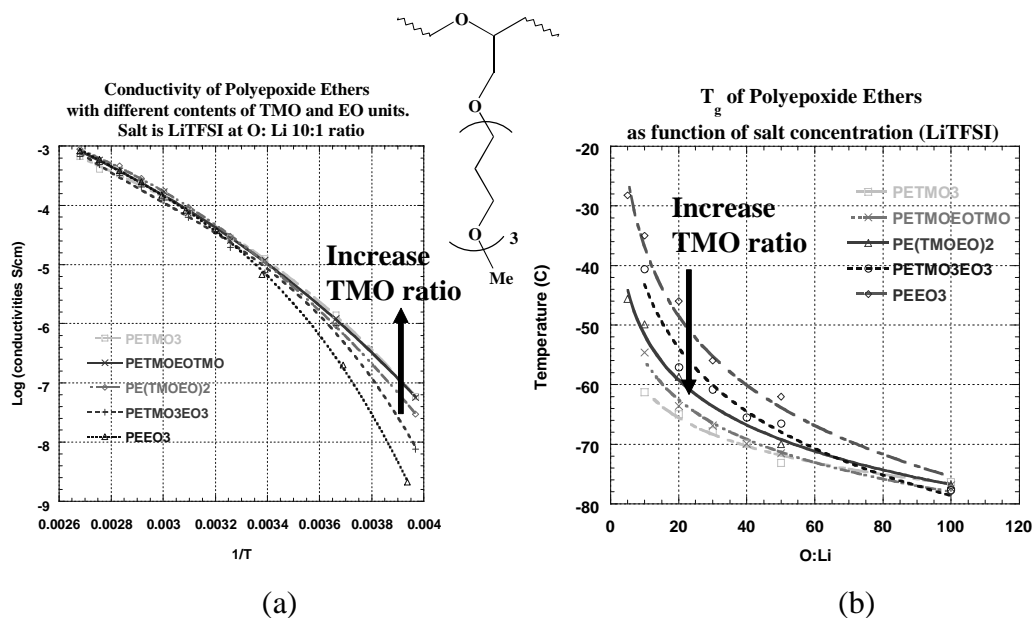


Figure 2. Effect of polymer structure on (a) Conductivity and (b) Glass Transition Temperature ( $T_g$ ) as a function of salt concentration.

Although the effects of concentration profiles may be alleviated by structural changes in polymer and salt, it is clear that the most attractive solution is to synthesize polyelectrolytes with a lithium transference number of one in order to completely avoid the salt concentration profiles. The comb branch structure appears to offer the best hope of achieving a polyelectrolyte with a satisfactory conductivity. It has been shown by modeling that a conductivity of  $10^{-4}$  S/cm at 25°C will provide EV performance[1] and this is the goal. The polyelectrolyte must not only possess good conductivity and hence have a low  $T_g$  but also must have sufficient mechanical strength to inhibit dendrite growth and be chemically stable to both lithium metal and metal oxides at 3.5-4.0 volts versus lithium. The polymer must also have sufficient flexibility to incorporate filler material such as carbon black which will decrease the mobility of the polymer side chains.. Figure 3 is a schematic representation of the polymer architecture that is envisioned as being ideal for the purpose. It consists of a cross-linked comb branch material with the anions ( $X^-$ ) attached to the ends of the side chains and the side chains themselves may contain appropriate

solvating groups for lithium ions such as EO or TMO. The structure is very similar to that of fuel cell polyelectrolyte membranes and one can easily envision exchange of  $H^+$  for  $Li^+$

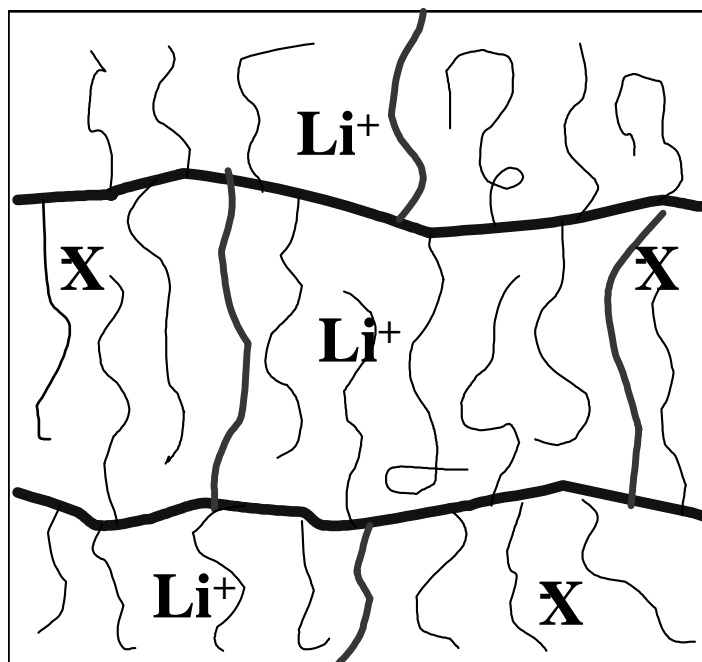


Figure 3. Schematic of ideal polyelectrolyte structure for lithium batteries.

### **Polyelectrolyte Membrane Synthesis and testing.**

Figure 4 shows the structures of several anions fixed to side chains that are of interest. The sulfonated acrylate ether systems (4a) are synthesized by simple radical polymerization of the sulfonated monomer together with acrylate ether monomers to produce polymers with different concentrations of ions[7]. The conductivities of these materials are shown in Figure 6 for different concentrations of ions. The glass transition temperatures ( $T_g$ ) were measured to be  $-62^\circ\text{C}$ ,  $-59^\circ\text{C}$  and  $-54^\circ\text{C}$  for 80:1, 40:1 and 20:1 respectively. The anions could also be fixed to the polymer by means of a grafting reaction which is shown in Figure 5. The chemistry here is a variation of hydrosilylation chemistry commonly used in polymer cross-linking[8] and indeed this is also used to cross-link the membrane. This method was used to graft both the sulfonate group in Figure 4a and the ditrifluoromethylsulfonylmethide group in Figure 4 b on to a polyepoxide prepolymer. The conductivities of the latter polymer were about half an order of magnitude higher than those of the polyacrylate materials shown in Figure 6 while Figure 7 shows the conductivities of grafted sulfonate polyelectrolytes. It is immediately obvious that the conductivity of the grafted materials considerably lower than those of the sulfonated polyacrylate ethers. This result is unexpected as the acrylate backbone would be expected to increase the  $T_g$  and hence decrease the conductivity. However, on examination of the prepolymer and the grafted polyelectrolyte by DMA it is clear that there is considerable non-uniformity in the material. This appears to result from the non-random nature of the co-polymerization of

monomer with cross-link agent (allyl glycidyl ether). This is corrected by use of a better cross-linking agent and better co-polymerization conditions.

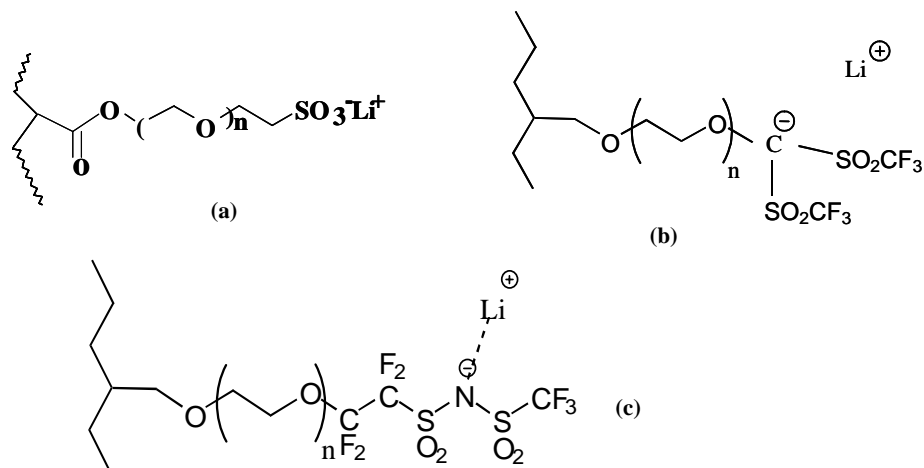


Figure 4. Structures for fixing anions on side chains of comb branch polymers

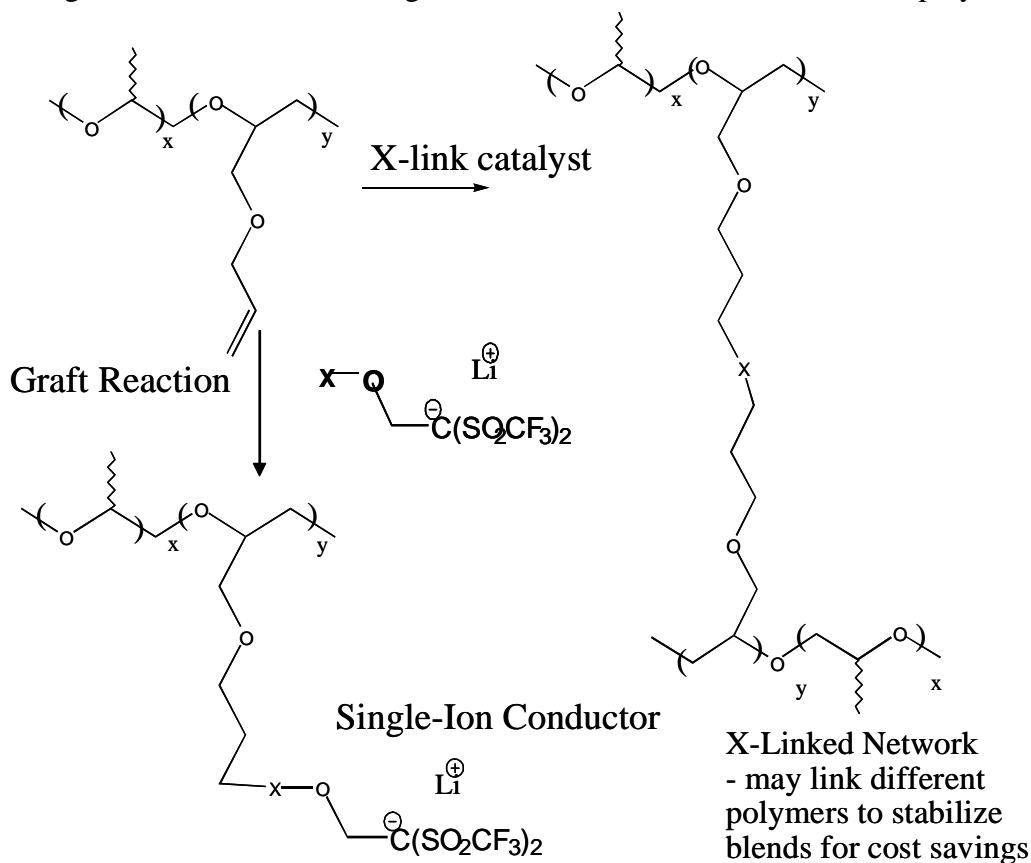


Figure 5. Hydrosilylation Chemistry is used to graft anion structures on to pre-polymers and to cross-link the membrane for mechanical properties.

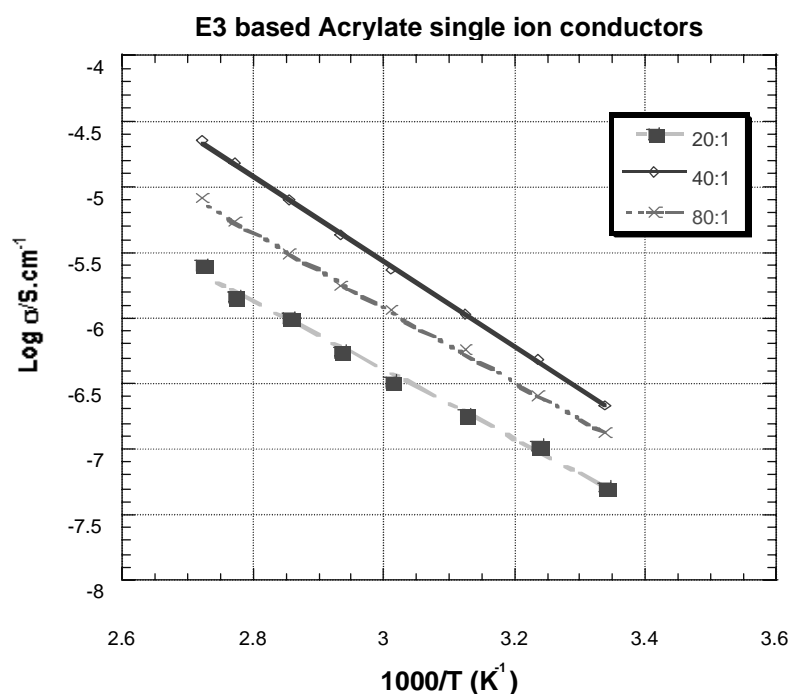


Figure 6. Conductivities of Lithium salts of Sulfonated Polyacrylate Ethers

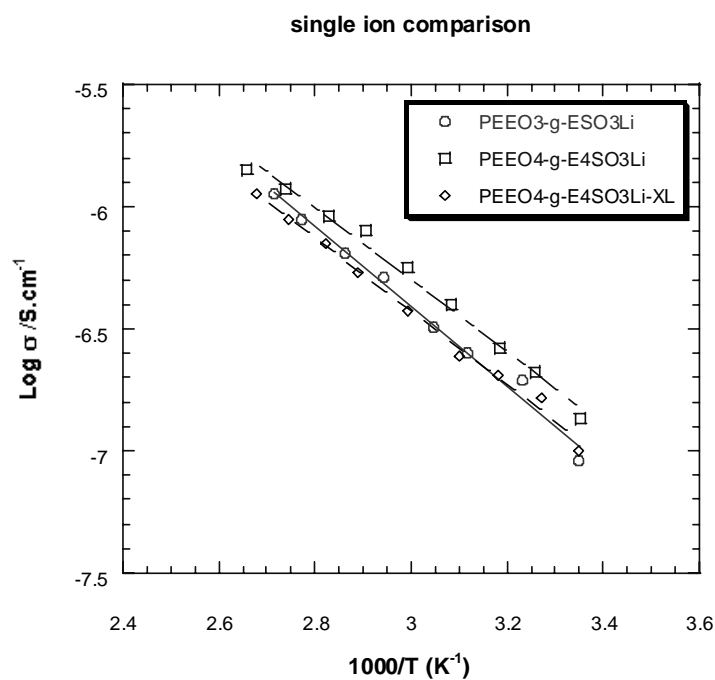


Figure 7. Conductivities of Lithium salts of grafted sulfonate polyethers including the effects of cross-linking the membrane.

The polymers formed by graft reaction to give the methide group (Figure 4b) have been tested in lithium-lithium half-cells. Application of current at  $50\mu\text{A}/\text{cm}^2$  at  $85^\circ\text{C}$  was carried out for a total of  $8\text{ coulombs}/\text{cm}^2$  and no concentration polarization was observed. It was noted that the membrane failed after two cycles due to apparent reaction with lithium metal. This is thought to be due to the use of siloxane to perform the graft reaction. Work is continuing on improving the stability of the membranes to lithium metal.

## Conclusions.

It can be seen that the conductivities of the polyelectrolytes prepared to date fall short by at least two orders of magnitude. However, the sulfonated polyacrylate ethers used for Figures 6 and 7 are not optimized for a number of factors. These are:

- 1) ion concentration; the optimum has been predicted to be  $\sim 40:1 [\text{O}]:[\text{Li}^+]$ [9] and this has been confirmed for these sulfonated polyacrylate ethers where a decrease of the lithium ion concentration yields nearly an order of magnitude increase in conductivity
- 2) Side chain length; the optimum side chain length for polymer electrolytes has been shown to be 5-6 EO or TMO unit and preliminary calculations on polyelectrolytes indicate that this is the ideal length for the pendant side chain containing the anion group.
- 3) carbon-linker; recent measurements have demonstrated the greater flexibility of TMO vs. EO units in both comb branch and linear polymers resulting in lower  $T_g$  values for the TMO-containing polymers at high salt concentrations. Introduction of the TMO units into the chains that hold the ions is expected to increase mobility for the ions and increased conductivity.
- 4) anion identity; it has been shown that replacement of sulfonate with triflate leads to increased conductivity[10]. Substitution of sulfonate with trifluoromethylsulfonyl imides and methides is expected to yield further gains in conductivity. Thus, a roadmap exists to improve conductivity by at least 2 orders of magnitude over that shown in Figure 6.
- 5) uniformity; more random co-polymerization will lead to better conductivity.
- 6) stability: the stability of these materials to lithium metal is still not proven.

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